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Complete unbinding and quasi-long-range order in lamellar phases

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Lamellar phases of lyotropic liquid crystals can be swollen by addition of solvent. Such a process, which leads to a strong increase of the mean interlamellar separation $\bar{l}$, can be viewed as a phase transition, termed complete unbinding. Starting from the microscopic interaction for a pair of lamellae, we derive an effective model for the multilayer phase. We predict a power-law increase of $\bar{l}$, and show that the system exhibits quasi-long-range translational order characterized by an exponent X_m, which is either universal or, for sufficiently long-range repulsive interactions, depends on molecular details.

I. INTRODUCTION

One of the simplest of the large variety[1] of different structures found in solutions of amphiphilic molecules is the so-called lamellar phase in which the molecules form roughly parallel layers separated by layers of solvent. Lamellar structures have recently regained the attention of the physicists from both experimental[2,3] and theoretical[4] viewpoints. Experimental studies have been carried out in lyotropic liquid crystals: in binary systems, such as phospholipid bilayers alternating by water[5] [Fig. 1(a)], or in (quasi) ternary solutions where the surfactant films separate two different solvents usually water and oil[2,3] [Fig. 1(b)]. The second class of experiments is more robust since the lamellar structure can be swollen either by adding water or oil: in the latter case unusually large spacings up to 6500 Å have been observed.[3]

A recently developed theory[6] describing the interactions of two fluctuating membranes predicted the existence of *critical unbinding transitions* between a state in which the membranes are bound together to a state in which they are completely separated. Here, we address the issue of how this theory can be applied to the case of lyotropic liquid crystals, and to the swelling of lamellar structures.

Toward those ends, we generalize the model of Ref. 6 to a *stack of fluctuating membranes* (or lamellae), and to *constrained systems.* The latter notion arises because in the process of swelling the separation between the lamellae is usually determined by the composition of the mixture, a situation different from the case in which the membranes are allowed to equilibrate in excess solvent, so that their mean separation is directly determined by the intermembrane forces.

In Sec. II we first consider two lamellae interacting via molecular forces, such as van der Waals attraction and short-range hydration repulsion, in the presence of an external constraint, such as an external pressure. We argue that the process of swelling is equivalent to relaxing this constraint, and can also be viewed as an unbinding transition. However, this new transition, which we call *complete unbinding,* is quite different from the *critical unbinding* transition.[6] While the former is again driven by thermal fluctuations, their effect is much weaker and can be accurately taken into account by introducing an effective *entropic (steric) repulsion* between the membranes.[7] We show that complete unbinding can be described by *an effective Gaussian model.*

In Sec. III we extend these results to the case of a stack of lamellae. The effective Gaussian model leads naturally to the prediction of *quasi-long-range order* in the lamellar structure. If the interactions are sufficiently short-ranged, the characteristic exponent X_m which describes the decay of correlations of the lamellae does *not* depend asymptotically on the mean separation $\bar{l}$, between the layers and is, in fact, a pure number. These results seem to be consistent with recent experiments in (quasi) ternary solutions, where the quasi-long-range order manifests itself in power-law decay of the scattering intensities.[2,3]

Sections II and III describe the case of electrically neu-

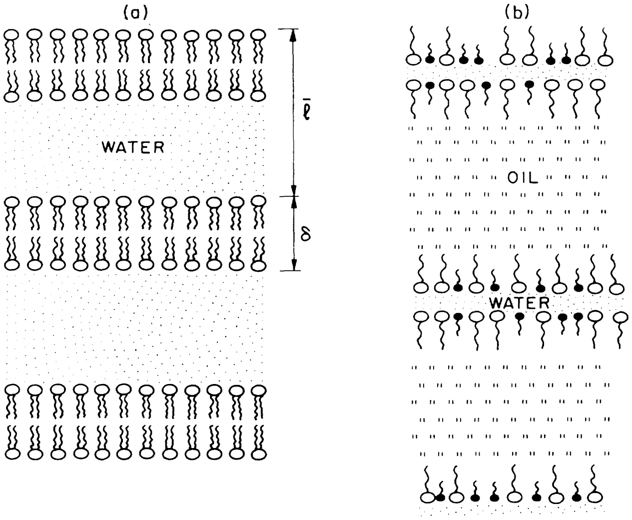

FIG. 1. A schematic view of the lamellar phases of lyotropic liquid crystals. (a) Binary system. (b) Quasiternary system. In the latter case one can swell the structure either by addition of water or oil. $\bar{l}$ is the mean spacing between the lamellae, δ is the thickness of the layers.

tral lamellae. The case of *charged* layers is taken up in Sec. IV, with emphasis on the interesting situation in which the lamellae interact via long-range, unscreened repulsive forces. Such interactions drastically change the critical properties of complete unbinding, as well as the power-law decay of the scattering peaks. In addition the presence of such long-range interactions can lead to first-order transitions among two different lamellar structures. In the concluding section (V), we discuss the relevance of our theory to experiments in lyotropic liquid crystals.

II. TWO LAMELLAE UNDER CONSTRAINT

The effective interaction between two lamellae resulting from the microscopic forces between the various molecules are complicated and despite many experimental and theoretical studies,[8] are not understood thoroughly.[9] We shall therefore concentrate on the generic situation in which the free energy per unit area or the interaction potential

$$V_0(l) = V_R(l) + V_A(l) \tag{1}$$

between two neighboring lamellae at spacing l has a repulsive part $V_R(l)$, and an attractive part $V_A(l)$, which dominates for large l.[6] The attractive part is usually due to the van der Waals interaction.[10] For large l, one has

$$V_A(l) \approx -W\delta^2/l^4 \ , \tag{2}$$

where W is the Hamaker constant,[11] and δ the typical thickness of the lamellae which is assumed small compared to the mean separation $\bar{l}$. If unscreened electrostatic interactions, resulting from charges on the lamellae are present, one must add a repulsive long-range part to $V_0(l)$ given by[12]

$$V_{\mathrm{el}}(l) \approx E/l \ , \tag{3}$$

for sufficiently large l. We postpone this case to the end of the paper.

In many experimental cases,[3,5] the lamellar phase does not coexist with a bulk solvent phase but rather, the lamellar structure is progressively swollen as oil or water is added. This is accounted for by including a pressurelike term in the interaction potential:

$$V(l) = V_0(l) + Pl \ . \tag{4}$$

The parameter P can be viewed as a Lagrange multiplier if the mean spacing between the lamellae is determined by the total volume fraction of solvent. By increasing the amount of solvent one decreases this *external constraint*, and thus $P \to 0$. Alternatively, P may represent the external osmotic, mechanical, or vapor pressure applied to the lamellar system in equilibrium with a reservoir of solvent.[10]

The interaction potential $V(l)$ is the free energy per unit area for two *planar* membranes *which are at a constrained distance*. Undulations of the membranes give rise to an elastic contribution to the free energy which leads to the effective Hamiltonian[6]

$$\mathcal{H}[l(\mathbf{x})] = \int d^{d-1}x[\tfrac{1}{2}\kappa_0(\nabla^2 l)^2 + V[l(\mathbf{x})]/k_B T \ , \tag{5}$$

where κ_0 is the rigidity constant, and a high-momentum cutoff $\Lambda \sim 1/\delta$ is implicitly included. This model embodies several simplifying assumptions: it neglects finite-size effects, highly curved configurations of the lamellae, internal degrees of freedom of the layers, etc. In addition it does not account for other forms of aggegation such as micelles or vesicles. From an experimental point of view this could be an oversimplifying assumption, as we discuss in the end of this paper.

We aim to describe the *process of swelling of the lamellae*, as has been observed, for instance, by Larche *et al.*[3] in experiments on extremely dilute lyotropic liquid crystals. Thus we take the potential $V(l)$ in the form (4) and study the limit $P \to 0$. We have recently shown[6] that for two membranes or lamellae under no external constraint, i.e., $P = 0$, a *critical unbinding transition* can occur between a state in which the lamellae are bound and a state in which they are completely separated. This critical transition is driven by fluctuations. For a potential $V(l)$ of the form (1) and (2) (and $P = 0$) the critical unbinding transition takes place in three-dimensional systems at a *nonzero* value of the Hamaker constant $W_c > 0$, for $0 < W < W_c$ the two membranes are completely unbound even though their molecular interaction has a minimum at a finite distance l. This is an example of unbinding in the strong-fluctuation regime. This regime contains all interaction potentials $V(l)$ such that,[6] for large l,

$$V(l)l^{\tau} \approx 0 \ , \tag{6}$$

with

$$\tau = 2(d-1)/(5-d) \ . \tag{7}$$

Suppose now that one approaches $P = P_c = 0$ with $W < W_c$, as shown in Fig. 2. Then, P is the only relevant scaling field. On the other hand, at the critical point $(W, P) = (W_c, 0)$ there are two relevant fields: the "pressure" P and the critical-point deviation, $W - W_c$, of the Hamaker constant.[13] In both cases, the mean separation

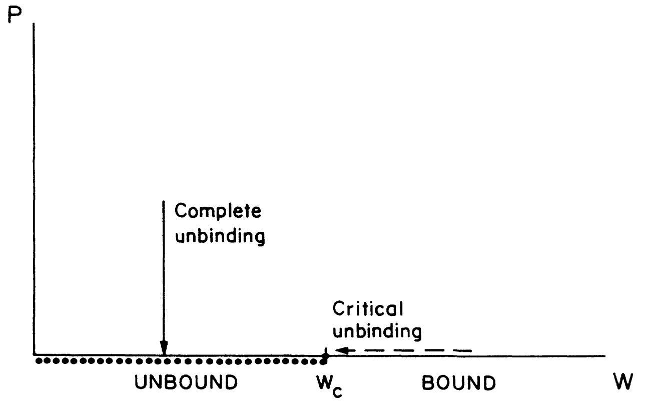

FIG. 2. The swelling of the lamellar phase can be viewed as the limit $P \to 0$, where P is a pressurelike variable. For values of the Hamaker constant W smaller than the critical value W_c complete unbinding takes place. In this (P, W) diagram the critical unbinding transition corresponds to the approach of $(W, P) = (W_c, 0)$.

between lamellae diverges asymptotically for $P \rightarrow 0$, with a power law characterized by a new exponent ψ:

$$\bar{l} \sim P^{-\psi} , \tag{8}$$

as $P \rightarrow 0$. For the slightly generalized interface potential

$$V(l) = V_R - W\delta^2/l^4 + Pl^q , \tag{9}$$

we find that

$$\psi = \zeta/[4-(2-q)\zeta] , \tag{10}$$

with

$$\zeta = (5-d)/2 . \tag{11}$$

Thus, in particular, for $q=1$ in the physical, three-dimensional case,

$$\psi = 1/3 \quad (d=3) . \tag{12}$$

The result (8) is derived from a self-consistency argument.[14] We put $l = \bar{l} + \phi$, where $\bar{l}$ is to be determined, and build a field theory for ϕ with the potential

$$\bar{V}(\phi) = V(l) - V(\bar{l}) = \sum_{n \geq 1} \frac{1}{n!} v_n \phi^n . \tag{13}$$

The $v_n = v_n(P,\bar{l})$ represent the perturbation theoretic "vertices." Now, we express $\bar{l}$ in terms of the correlation lengths $\xi_\perp$ and $\xi_\parallel$ which describe the fluctuation of the lamellae,

$$\bar{l} \sim \xi_\perp \sim \xi_\parallel^\zeta , \tag{14}$$

with ζ given by Eq. (11).

From the form (13) for the potential $V(l)$ it follows that all vertices vanish for $P \rightarrow 0$, as $v_n \sim P\bar{l}^{q-n} \sim P\xi_\parallel^{(q-n)\zeta}$. Now, let us consider the Fourier transform of the two-point correlation function

$$\tilde{G}(k) = \int \frac{d^{d-1}x}{(2\pi)^{d-1}} e^{i\mathbf{k}\cdot\mathbf{x}} \langle \phi(\mathbf{x})\phi(0) \rangle . \tag{15}$$

One can show[14] that any Feynman diagram of the perturbation expansion for $1/\tilde{G}\ (k=0)$ is proportional to $\xi_\parallel^{-4}(P\xi_\parallel^{\zeta q-1+d})^N$, where N is the number of vertices which appear in the Feynman diagram. Self-consistency then requires $1/\tilde{G}(k=0) \sim \xi_\parallel^{-4}$ which, together with the scaling relation (14) yields (8) and (10). Further, one finds the scaling form

$$1/\tilde{G}(k) = \xi_\parallel^{-4}\Omega(k\xi_\parallel) = \xi_\parallel^{-4}[\Omega_0 + \Omega_2(k\xi_\parallel)^2 + \Omega_4(k\xi_\parallel)^4 + \cdots] . \tag{16}$$

The expansion coefficients Ω_n $(n=0,2,4,\ldots)$ represent sums of Feynman diagrams which all give a finite contribution for $d \leq 5$ even when the cutoff Λ in (5) goes to infinity. It is interesting to note that one recovers $d < d_2 = 3\frac{2}{3}$ as a condition for the self-consistency of this approach.

The scaling form (16) has important consequences. First, it shows that the k^2 term which might be regarded as a *surface tension* contribution has a prefactor $\sim \xi_\parallel^{-2}$, which vanishes at the transition. Furthermore, at the transition point, with $\xi_\parallel = \infty$, the scaling form (16) implies that

$$\Omega(x) \approx \kappa x^4 \tag{17}$$

for large x, which leads to

$$1/\tilde{G}(k) = \kappa k^4 \quad (\xi_\parallel = \infty) . \tag{18}$$

This shows that there is no anomalous decay of the correlation function of the two lamellae when the transition point $P=0$ is approached.[16] The only effect of the interactions is to change the rigidity coefficient κ_0 to an effective rigidity κ. Therefore, we can use an effective Gaussian model to describe the separation of the lamellae. Let us consider the three-dimensional case, where (14) can be written more precisely as

$$\bar{l} = c_0(k_B T/\kappa)^{1/2}\xi_\parallel \quad (d=3) . \tag{19}$$

Here, c_0 is a numerical constant of order unity. Then the effective Gaussian Hamiltonian for two lamellae is given by

$$\mathcal{H}_G[\phi] = \int d^2x [\tfrac{1}{2}\kappa(\nabla^2\phi)^2 + \tfrac{1}{2}\kappa\xi_\parallel^{-4}\phi^2]/k_B T , \tag{20}$$

where κ is the rigidity constant renormalized by the interaction.

So far, we have tacitly assumed that the interaction potential $V(l)$ has only one minimum for $P=0$. However, one expects that, in the strong fluctuation regime, the fluctuations of the lamellae are so large that they can overcome barriers between two competing minima. This expectation is indeed confirmed by the results of a functional renormalization group calculation.[6,17] We find that the critical behavior for potentials $V(l)$ with two minima which are separated by a small barrier is governed by the same fixed point as for potentials with only one minimum. Thus, for $P=0$, and for potentials $V(l)$ in the strong fluctuation regime satisfying (6), a first-order transition can only occur for a sufficiently deep minimum.[18] By continuity, we expect this to be also valid for the approach to complete unbinding, e.g., for $P > 0$.

III. STACK OF LAMELLAE

Now, we consider a stack of lamellae and describe the interaction of each pair of nearest neighbors within this stack by the Hamiltonian (5). Then we take the continuum limit, and introduce a coarse-grained displacement variable $u(x,z)$ which depends on z in a continuous way. In this way, we obtain the effective Gaussian model

$$H_G = \int d^2x dz \left[\tfrac{1}{2}B \left[\frac{\partial u}{\partial z} \right]^2 + \tfrac{1}{2}K(\nabla^2 u)^2 \right] /k_B T , \tag{21}$$

with

$$B \equiv \kappa\bar{l}/\xi_\parallel^4 = c_0^4(k_B T)^2/\kappa\bar{l}^3; \quad K \equiv \kappa/\bar{l} , \tag{22}$$

where the scaling relation (14) has been used (for $d=3$). A model analogous to this has been introduced in the context of smectic liquid crystals.[19] It leads to the prediction of quasi-long-range translational order characterized by the algebraic decay of correlations with exponent

$$X_m = k_B T q_m^2 / 8\pi (KB)^{1/2} , \tag{23}$$

where $q_m = 2\pi m / \bar{l}$ $(m = 1,2,\ldots)$. The quasi-long-range order can be observed by analyzing the power-law scattering intensity peaks.[3,20]

$$S(q_z) \sim (q_z - q_m)^{-(2-X_m)} . \tag{24}$$

At the approach to complete unbinding, because of the particular behavior of the effective elastic constants B and K, as given by Eq. (22), the exponent X_m is given by

$$X_m = \pi m^2 / 2c_0^2 , \tag{25}$$

and is therefore a pure number. In particular, it does *not* depend on the mean separation $\bar{l}$, when $\bar{l}$ is large, i.e., on approach to complete unbinding.

In practice, there is a correction to (25) resulting from the finite thickness, δ, of the membranes.[21] If one neglects the lateral variations of δ, then a simple geometrical consideration leads to the effective elastic coupling constants

$$B = \kappa \bar{l} / \xi_{\parallel}^4 = c_0^4 \bar{l} (k_B T)^2 / \kappa (\bar{l} - \delta)^4, \quad K = \kappa / \bar{l} , \tag{26}$$

where $\bar{l}$ is now the period of the structure. When these formulae for the elastic constants are inserted into (23), one obtains

$$X_m(\delta) = (\pi m^2 / 2c_0^2)(1 - \delta/\bar{l})^2 , \tag{27}$$

an expression which seems to be confirmed by recent experiments.[21] For small ratios $\delta/\bar{l}$ this formula reduces to Eq. (25). In fact the experiment by Safinya *et al.* shows that X_m comes close to its asymptotic value for a spacing of the order of 200 Å.

For smectic liquid crystals, it has been shown[22] that higher-order anharmonic terms in the gradients of u should be included in (20). The form of these terms is, in fact, dictated by symmetry. The anharmonic terms have been shown to be important for wavelengths $1/(q_z - q_m)$ large compared to a crossover length z^*.[22] In the case considered here, this length scale is given by

$$z^* \simeq c_0^2 \left[\frac{k_B T}{\kappa} \right] \frac{\delta^2}{\bar{l}} \exp \left[\frac{128\pi}{5c_0^2} \left[\frac{\kappa}{k_B T} \right]^2 \right] \tag{28}$$

In lyotropic liquid crystals, the rigidity constant is expected to be $k_B T \lesssim \kappa \lesssim 100\ k_B T$. Therefore, at room temperatures and for $c_0 \simeq 1$, Eq. (28) leads to $z^* > 10^{35} \delta^2 / \bar{l}$, which is much larger than the size of the experimentally studied systems. Because of the exponential dependence of z^* on c_0 and κ, the anharmonic effects could easily become important, e.g., for $\kappa \simeq 0.1\ k_B T$, or $c_0 \simeq 5$.[27] Note, however, that one should be careful in applying the result (28) to the case of lamellar system because of the singular behavior of the elastic constant B and K.

IV. ELECTROSTATIC INTERACTIONS

Until now, we have assumed, that the electrostatic interactions do not play any important role, at least in (quasi) ternary lyotropic liquid crystals which are swollen by the addition of oil. If, however, on approach to complete unbinding, the swelling of lamellae is not governed by thermal fluctuations, but rather by an unscreened long-range electrostatic repulsion (3), then Eq. (25) must be modified.

In this case, the approach to the unbound phase as $P \to 0$ is described by mean-field theory which leads to $\bar{l} \sim P^{-1/2}$ and $\xi_{\parallel} \sim P^{-3/8}$. This implies effective elastic constants vanishing as $B \sim 1/\bar{l}^2 \sim P$ and $K \sim 1/\bar{l} \sim P^{1/2}$, and therefore the exponent

$$X_m \simeq k_B T / (E \kappa \bar{l})^{1/2} \sim P^{1/4} \tag{29}$$

depends explicitly on the mean lamellar spacing $\bar{l}$ and vanishes as $P \to 0$.

Furthermore, since mean-field theory is valid here, we conclude that the separation of two lamellae now changes in a discontinuous way if the potential has two competing minima. Hence, in the presence of long-range electrostatic repulsions, it would be easier to find physical systems in which two lamellar phases which differ in their spacing $\bar{l}$ coexist. More complicated structures could also be possible in which the mean separation $\bar{l}$ varies *within* a lamellar phase. For this, one would have to take further neighbor interactions into account in order to determine the structure.

V. CONCLUSIONS

Let us now return to the generic case without electrostatic interactions (1) and to the results (8) and (10). These expressions can also be obtained in a heuristic way by *assuming* that the thermal fluctuations induce the effective steric repulsion

$$V_{\text{st}} \sim (k_B T)^2 / \kappa \bar{l}^2 \quad (d = 3) \tag{30}$$

between lamellae, as postulated by Helfrich,[7] and then using, for instance $B = \bar{l} (d^2 V_{\text{st}} / dl^2)_{\bar{l}}$. Indeed, such an approach has been adopted by several authors.[3,7] But note, first, that the steric repulsion alone cannot lead to a finite separation $\bar{l}$ of the lamellae: one has also to include the molecular potential with its attractive part $V_A(l)$ of the pressure-like term, Pl. Second, it is important to realize that the simple superposition of the molecular potential $V(l)$ and the effective entropic interactions $V_{\text{st}}(l)$ is not correct in general. Indeed, this reasoning is certainly not valid for the critical unbinding transition in three dimensions:[6] even to predict the existence of a continuous unbinding transition it is necessary there to carry out a full statistical treatment of the model. One may therefore ask why, in the present case, the simple-minded derivation gives the correct asymptotic behavior. This arises from the fact that for the complete unbinding transition the phase boundary at $P = P_c = 0$ cannot be shifted by fluctuations. As a result, one has only two scaling regimes for complete unbinding: a mean-field regime for $d > d_2 = 3\frac{1}{3}$, and a weak fluctuation regime for $d < d_2$. Both regimes are in principle accessible experimentally: in the presence of electrostatic repulsion (3), one would probe the mean-field regime, whereas in the absence of such interactions, the weak-fluctuation regime is entered.

For sufficiently weak attraction between the lamellae our theory predicts that the mean separation $\bar{l}$ can increase without limits when a solvent is added. However, the theoretical description of the swelling of the lamellae presented here does not take into account other forms of aggregation such as micelles, vesicles, hexagonal structures, etc. It also ignores the possible formation of defects. Such structures can have a lower free energy than the lamellar phase. In this case, the swelling of lamellae could still be large, but would eventually be limited, in thermal equilibrium, by the appearance of a new amphiphilic phase. Even then one could still study the approach to complete unbinding along the *metastable* branch of the lamellar phase if the time scale which governs the decay into new structures is sufficiently large.

The results described in this paper also depend crucially on the assumption that the thermal fluctuations of the lamellae are controlled by their curvature energy. Indeed, by analogy with the smectic liquid crystals one can argue on the basis of symmetry arguments[19,22] that a surface tension-like term is absent in the effective Hamiltonian (21). On the other hand, one expects that, in some cases, a nonzero tension of the lamellae can be induced by the boundary conditions,[23] fast exchange of molecules with other aggegates,[24] or other factors.

The presence of a surface tension term, $\sigma(\nabla l)^2$, in the effective Hamiltonian (5) and (21) would have several interesting consequences: (i) it would introduce additional scales $\lambda_\perp = (k_B T/\sigma)^{1/2}$ and $\lambda_\parallel = (\kappa/\sigma)^{1/2}$ for the perpendicular and parallel correlations, respectively; (ii) for $\bar{l} \ll \lambda_\perp$, the steric entropic repulsion would still be given by Eq. (30), but for $\bar{l} \gg \lambda_\perp$, it would be replaced by a Gaussian tail;[25] (iii) the scattering intensity would exhibit Bragg peaks since the Debye-Waller factor would no longer vanish.[26]

In conclusion, we have shown that in some situations the swelling of lamellar liquid crystals can be considered as a new phase transition termed complete unbinding. The quantitative predictions of our model, such as the behavior of the mean separation between lamellae $\bar{l}$, or the existence of quasi-long-range order characterized by the exponent X_m, can be checked experimentally.

Note added in proof. Recent experiments by D. Roux and C. Safinya and collaborators have shown that in the presence of unscreened electrostatic interactions, the effective exponent X_M indeed decreases with $\bar{l}$, in qualitative agreement with our prediction (29). For details, see D. Roux, Proceedings of Les Houches Conference "Amphiphilic films," February 1987 (to be published).

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[1] See, e.g., *Surfactants in Solution*, Vol 1–3, edited by K. L. Mittal and B. Lindman (Plenum, New York, 1984).

[2] J. M. DiMeglio, M. Dvolaitzky, L. Leger, and C. Taupin, Phys. Rev. Lett. **54**, 1686 (1985).

[3] F. C. Larche, J. Appel. G. Porte, P. Bassereau, and J. Marignan, Phys. Rev. Lett. **56**, 1700 (1986); C. R. Safinya, D. Roux, G. S. Smith, S. K. Sinha, P. Dimon, N. A. Clark, and A. M. Bellocq, Phys. Rev. Lett. **57**, 2718 (1986).

[4] O. Parodi, in *Colloïdes et Interfaces.*, edited by A. M. Cazabat and D. Langevin, (Editions de Physique, Paris, 1983. p. 355; see also V. A. Parsegian and E. Evans (unpublished).

[5] See, e.g., W. Harbich and W. Helfrich, *Chem. Phys. Lipids* **36**, 39 (1984); L. J. Lis, M. McAlister, N. Fuller, R. P. Rand, and V. A. Parsegian, Biophys. J. **37**, 657 (1982).

[6] R. Lipowsky and S. Leibler, Phys. Rev. Lett. **56**, 2541 (1986).

[7] W. Helfrich, Z. Naturfosch. **33a**, 305 (1978).

[8] J. N. Israelachvili, *Intermolecular and Surface Forces,* (Academic, Orlando, 1985).

[9] D. F. Evans and B. W. Ninham, J. Phys. Chem. **90**, 226 (1986).

[10] A review is R. P. Rand, Ann. Rev. Biophys. Bioeng. **10**, 277 (1981).

[11] Note that in the systems considered here the van der Waals interaction between two lamellae is always attractive (see Ref. 6).

[12] See the *Langmuir equation* in Ref. 8.

[13] In experimental systems it can be easier to control other physical parameters such as the elastic constant κ (Ref. 8), the thickness δ of the lamellae [D. Roux and C. Safinya (private communication)], etc., rather than the value of the Hamaker constant W. The scaling field $W - W_c$ should then be replaced by an appropriate linear combination of the deviations: $\kappa - \kappa_c, \delta - \delta_c$, etc.

[14] D. M. Kroll, R. Lipowsky and R. K. P. Zia, Phys. Rev. B **32**, 1862 (1985).

[15] By the arguments used for the critical unbinding transition (Ref. 6), one can show that for complete unbinding the first relation $\bar{l} \sim \xi_\perp$ and the second relation $\xi_\perp \sim \xi_\parallel^{\zeta}$ hold for $d < d_2 = 3\frac{2}{3}$ and for $d < d_1 = 5$, respectively.

[16] Here, we assume that the fully renormalized rigidity constant remains positive at complete unbinding. This is true for the effective Hamiltonian (5) considered here.

[17] R. Lipowsky and M. E. Fisher, Phys. Rev. Lett. **57**, 2411 (1986).

[18] This is also suggested by analogy with wetting transitions. In the latter case, one can show for $d = 2$ that there are no first-order transitions in the strong fluctuation regime (Ref. 14).

[19] See, e.g., P.-G. de Gennes, *The Physics of Liquid Crystals,* (Oxford University Press, Oxford, 1974).

[20] A. Caillé, C. R. Acad. Sci. **274B**, 891 (1972).

[21] See C. R. Safinya, *et al.*, Ref. 3.

[22] G. Grinstein and R. Pelcovits, Phys. Rev. A **26**, 915 (1982).

[23] W. Helfrich (private communication).

[24] F. Brochard, P.-G. de Gennes, and P. Pfeuty, J. Phys. (Paris) **37**, 1099 (1976); R. E. Goldstein and S. Leibler (unpublished).

[25] M. E. Fisher and D. S. Fisher, Phys. Rev. B **25**, 3192 (1982).

[26] L. Gunther, Y. Imry, and J. Lajzerowicz, Phys. Rev. A **22**, 1733 (1980).

[27] F. Nallet and J. Prost, Proceedings of Les Houches Conference "Amphiphilic films," February 1987 (to be published).